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Conference paper

Patrick A. Figaroa*, Henk Miedema, Gert-Jan Euverink and Francesco Picchioni*

Functional polyketones for the removal of calcium and magnesium from water (part I): synthesis and chemical characterization

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Abstract: The aim of the present study was to design and synthesize a new class of compounds for the softening of hard water, i.e. for the removal of the divalent cations Ca^{2+} and Mg^{2+} . To that end, a class of alternating aliphatic polyketones (copolymers of ethylene and propylene with carbon monoxide, PK30) was functionalized with a variety of amines employing the Paal-Knorr reaction, a relatively straightforward reaction-route to synthesize functional polyketones. The amino groups included aliphatic and aromatic structures with a molecular weight ranging from 74.1 to 129.2 g/mol. Elemental analysis was used to establish the degree of functionalization, whereas ^1H -NMR spectroscopy was used to identify the molecular structure of the prepared polymers. Model compounds were used as reference for guiding structure determination and for studying the (relative) reaction kinetics.

Keywords: elemental analysis; ^1H -NMR spectroscopy; Paal-Knorr functional polyketones; POC-16.

Introduction

Scaling, i.e. the deposition of salts, notably those of Ca^{2+} and Mg^{2+} , can seriously compromise processes in water technology. For this reason, the mechanism of scaling, including strategies to treat or even prevent it, is an extensive field of research [1]. Ultimately, hard water can lead to complete failure of both industrial and domestic installations. The most widely used method to treat hard water is replacement of Ca^{2+} and Mg^{2+} by more soluble ones (e.g. Na^+) via ion exchange [2]. Although these ion exchange resins are quite effective, the regeneration of the resins results in a high Na^+ containing waste stream. From the environmental point of view it would be preferable to remove Ca^{2+} and Mg^{2+} simultaneously with an accompanying anion [3]. This way the Na^+ wash step could be omitted altogether. Functionalized polymeric materials offer this possibility.

Functionalized polymeric materials can be synthesized by the Paal-Knorr reaction [4]. This reaction has proven to be a straightforward reaction-route to synthesize functional polyketones [5], when compared to the cumbersome synthesis of other materials [6–15] including those recently published [3, 16, 17]. The Paal-Knorr reaction is a simple and inexpensive route for synthesizing novel polymeric resins bearing functional

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or multifunctional amino groups. The entire synthesis can readily be performed in the laboratory as well as on a larger scale [5, 18–22]. The resulting functional groups are in the form of primary, secondary or tertiary amino groups, either positioned on the backbone (i.e. pyrrole rings) of the polymer or as a side chain with additional nitrogen atoms. The reaction mechanism consists of pyrrole ring-formation by a double condensation reaction of a primary amino unit with a 1,4-dicarbonyl group on the polyketone. The resulting product is a functional polyketone bearing amino groups pending from the main chain of the polymer. The reaction is extremely sensitive to steric hindrance [23] as such, when reacting amino groups of different structure, the Paal-Knorr route offers the potential to prepare polymers with a controlled functional yield.

As starting material, we used an alternating aliphatic polyketone with 30 % ethylene and 70 % propylene content (PK30, MW 2670), which was functionalized with different kind of amino groups (Fig. 1).

The reaction can be easily carried out in bulk, with kinetics that does not require the use of a catalyst. The key feature of this reaction is the possibility to produce a large diversity of polyketones (i.e. in terms of specific type and number of amino groups present along the backbone), thereby anticipating a unique chemical structure-function relationship. The implication of this feature is that it allows fine-tuning of the performance according to each particular application. For example, PK30, bearing a piperazine amino group of functionality has proven to be an excellent chelator for metal ions [24].

The aim of the present study was to design and synthesize functional polyketones by means of the Paal-Knorr reaction. The amines functionalized with PK30 include four types of amino aliphatic-based structures, three types of amino aromatic-based structures and one type of carbon aliphatic-based structure. All amino groups are positioned as side chain pending from the polymer backbone and loaded with semi-aromatic pyrrole rings, and/or combinations with imine units. Products bearing both pyrrole rings and imine units depends strongly on the number of carbonyl units reacted. According to the Paal-Knorr reaction mechanism,

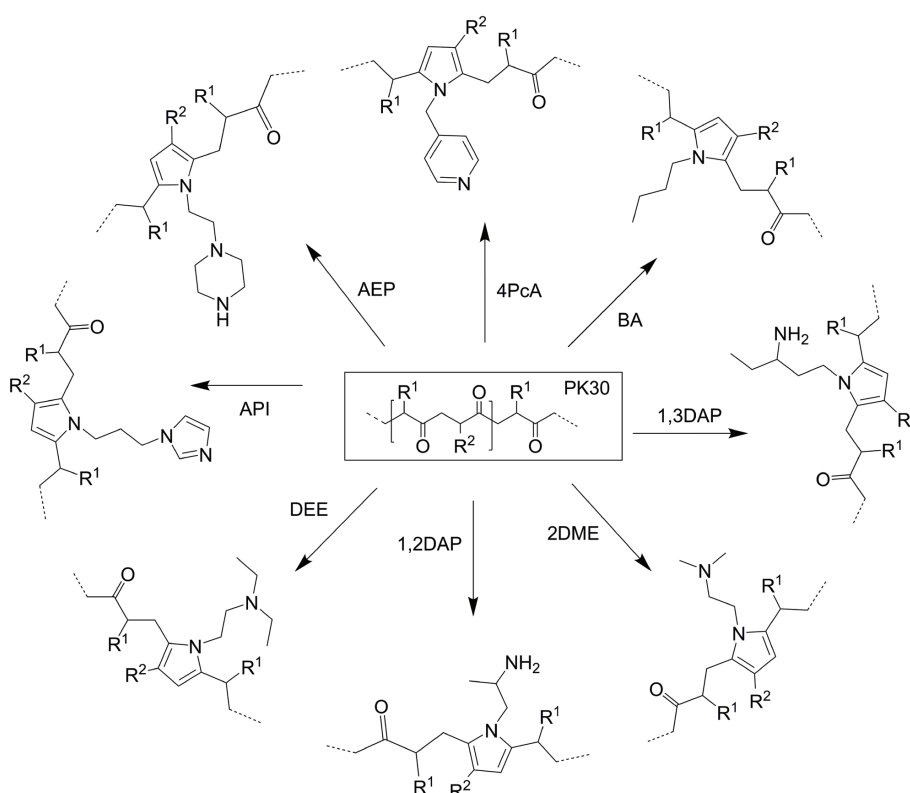


Fig. 1: Repeating units. PK30 modifications with amine: 1,2-diaminopropane (1,2DAP), 4-picolylamine (4PcA), 1,3-diaminopentane (1,3DAP), *N,N*-dimethylethylenediamine (2DME), *N,N*-diethylethylenediamine (DEE), 1-(3-aminopropyl)imidazole (API), 1-(2-aminoethyl)piperazine (AEP), butylamine (BA). *R* = 70 % CH₃ or 30 % H.

two carbonyl units are needed side by side to react into a stable pyrrole ring. Only when these units have reached maximum conversion, then the remaining single carbonyl units react as imine units. In this work, the binding affinity of Ca^{2+} and/or Mg^{2+} was aimed to correlate with the N of the amino groups in particular on the molecular regions of the functional polyketone.

Experimental

Reagents of choice

The amines including its functional groups chosen here (Fig. 1): 1,2DAP, 4PcA, 1,3DAP, 2DME, DEE, API, AEP and BA together with the model compounds reagent 2,5-hexanedione (2,5-HD) were all purchased from Sigma-Aldrich with purity grades $\geq 95\%$ and used without further purification. PK30, MW 2670, ter-polymer of carbon monoxide, 30 % ethylene and 70 % propylene content, was synthesized according to a previously reported protocol [25]. The abbreviations for the aliphatic type of amines are as follows: 1,2DAP; 1,3DAP; 2DME and DEE. The abbreviations for the aromatic type of amines are as follows: 4PcA, API and AEP. The carbon type of amine is abbreviated as BA.

Synthesis of the functional polyketones by the Paal-Knorr reaction

Functional polyketones with pyrrole rings incorporated in the backbone bearing amino (functional) groups pendant from the main chain were synthesized by reacting a class of low molecular weight polyketones with different kind of amines. The Paal-Knorr mechanism involves the reaction between a 1,4-dicarbonyl group and a primary amino unit and consists of three major steps: addition of the primary amino unit to the first carbonyl, addition/elimination and rearrangement steps (including the reaction with the neighboring carbonyl group), and stable product formation. The entire pathway consists of a flexible one-pot reaction, without the need of any catalyst, organic solvent or additives. The reaction can be carried out at mild conditions and the only by-product is water. In view of a maximal carbonyl conversion of about 80 % (due to statistical reasons) [5], an initial molar ratio of 0.8 between the amine and di-carbonyl groups along the backbone was firstly employed. This way the feasibility of the synthetic route was established. In a subsequent step the polymers were cross-linked. Without cross-linking the polymers collide into a clump in water because of intramolecular forces, most probably due to the hydrophobicity of the dominating nonpolar chains. Furthermore, the polymers solubilize during long-term exposure to water, even more so at elevated temperatures. Therefore, a carbonyl conversion of about 50 %, as determined by elemental analysis, was aimed for the first modification step to obtain a good “sandy” composition. This leaves roughly 30 % of the carbonyl groups originally present along the backbone for the cross-linking step. The functional polyketones were synthesized in quantities of 40 g PK30 by applying a one pot synthesis in the presence of the amines [5]. The reactions were carried out in a sealed 250 mL round bottom glass reactor with reflux condenser and U-type anchor impeller, positioned in an oil bath for temperature control. Process conditions were based on assuming an initial molar fraction of reactive 1,4-dicarbonyl groups in PK30 of 0.8 and 0.5 (see above), i.e. we anticipate that 80 % and 50 % of the reactive groups of PK30 should be converted. Prior to starting the reaction, 40 g of PK30 was pre-heated in an oil bath to a temperature of 110 °C. The amines were added drop-wise during the first 20 min of the reaction time, under a constant stirring speed of 500 rpm. The reaction time for PK30 with amine; 4PcA, 2DME, DEE, API, AEP and BA was 4 h. A shorter reaction time of 40 min was chosen for the modifications with 1,2DAP and 1,3DAP in order to prevent auto-cross-linking, given both molecules possess two amino units, albeit with different reactivity [5]. Unreacted amines were extracted into the water-phase by dissolving the functional polyketones in chloroform (Sigma-Aldrich, 99 %) and shaking conditions (e.g. for non-solid particles) and intensively washed with Milli-Q (e.g. for solid particles) at room temperature. Chloroform in the organic

phase was removed by vacuum rotary evaporation. After the purification steps, the functional polyketones were dried in a vacuum-oven-evaporator (100 mbar) at 40 °C, and left drying for at least 48 h to remove traces of water.

Characterization techniques

Elemental analysis

The degrees of carbonyl conversions were obtained from Elemental Analysis (EA) data, in particularly regarding the nitrogen content. EA of nitrogen in wt.% was performed with an Euro elemental analyzer (in duplo) by using approximately 2 mg of each dry prepared functional polyketone. The calculation of the conversions was explained in detail previously [26] and is given by:

$$X_{\text{co}} = \frac{2y}{2y + x} \cdot 100 \quad (1)$$

where x is the number of moles of the unreacted monomeric species and y the number of moles reacted monomeric units present in 100 g functional polyketone. For example, PK30 shown in Fig. 2, the chance that the R -group represents H or CH_3 is 30 % and 70 %, respectively.

The probabilities are thus defined here as $P_{\text{H}} = 0.3$ and $P_{\text{CH}_3} = 0.7$. Modification of PK30 with 4PcA is taken here as an example, yielding the polymer below (Fig. 3).

Since, for statistical reasons, the carbonyl conversion (X_{co}) cannot reach 100 %, in all cases $x \neq 0$. Notice that the product is not a block copolymer, but it displays the presence of the units outlined above randomly oriented. The X_{co} was calculated by EA, particularly using the nitrogen content (N expressed as wt.% of N in the sample) and given by Eq. 1. The amount of moles for the two monomeric units in 100 g of product, x and y can be calculated as follows. Consider 100 g of end product with N the amount of grams of nitrogen present in the sample. The amount of nitrogen moles (n_N) is then given by:

$$n_N = \frac{N}{M_N} \quad (2)$$

with M_N being the molecular weight of N (14 g/mol). The structure shown in Fig. 3 indicates that this particular repeating unit of 4PcA contains two N-atoms, implying:

$$y = \frac{n_N}{2} \quad (3)$$

Now that y is known, x can be calculated from the mass balance:

$$100 = x \times \overline{M}_x + y \times \overline{M}_y \quad (4)$$

where \overline{M} is the average molecular weight of the monomeric units, either the carbonyl (x) or the pyrrole (y) ones. The term average refers to the probability of R being 30 % H or 70 % CH_3 . Finding x requires the calcu-

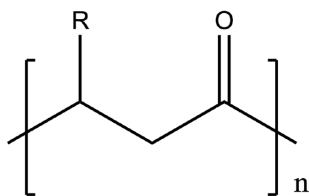


Fig. 2: Unreacted monomeric unit of PK30.

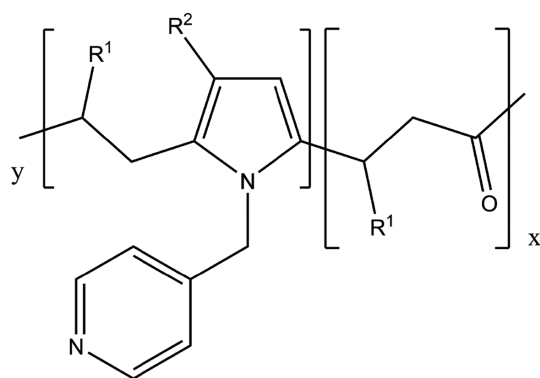


Fig. 3: PK30 modified with 4PcA. Reacted and unreacted monomeric units are represented as unit y and x , respectively.

lation of \overline{M}_y and \overline{M}_x first. The calculation of \overline{M}_x is straightforward. The molecular weight of the carbonyl repeating unit for R being H is 56 g/mol ($M_{C,R=H}$) and for R being CH_3 is 70 g/mol ($M_{C,R=CH_3}$). This leads to:

$$\overline{M}_x = P_H \times M_{C,R=H} + P_{CH_3} \times M_{C,R=CH_3} \quad (5)$$

The calculation of \overline{M}_y , on the other hand, is slightly more complicated since the repeating unit contains 2 R groups. It is assumed that the chances of 30 % and 70 % mentioned above are independent of the identity of the R -group on the same repeating unit. Suppose the probability for the 2 R 's to be both H denoted as $P_{H,H}$, for the first R to be CH_3 and the second H as $P_{CH_3,H}$, for the first R to be H and the second CH_3 as P_{H,CH_3} and finally for the 2 R 's to be both CH_3 as P_{CH_3,CH_3} . Because of the random distribution, one can write:

$$P_{H,H} = P_H \times P_H = 0.3 \times 0.3 = 0.09$$

$$P_{H,CH_3} = P_H \times P_{CH_3} = 0.3 \times 0.7 = 0.21$$

$$P_{CH_3,H} = P_{CH_3} \times P_H = 0.7 \times 0.3 = 0.21$$

$$P_{CH_3,CH_3} = P_{CH_3} \times P_{CH_3} = 0.7 \times 0.7 = 0.49$$

Obviously, for molecular weight calculations, it does not matter which one of the two R -groups is CH_3 or H. Therefore, $P_{CH_3,H}$ and P_{H,CH_3} can be combined $P_{CH_3,H} = P_{H,CH_3} + P_{CH_3,H} = 0.42$. This gives the following probabilities:

$$P_{H,H} = 0.09 \quad \overline{P_{CH_3,H}} = 0.42 \quad P_{CH_3,CH_3} = 0.49$$

$$\overline{M}_y = P_{H,H} \times M_{y,H,H} + \overline{P_{CH_3,H}} \times M_{y,CH_3,H} + P_{CH_3,CH_3} \times M_{y,CH_3,CH_3} \quad (6)$$

The calculation of \overline{M}_y can then be completed. In the example given above, the calculation of \overline{M}_y reads:

$$0.09 \times 184 + 0.42 \times 198 + 0.49 \times 212 = 204 \text{ g/mol}$$

Finally, the values of x and X_{CO} follow from Eq. 4 and Eq. 1, respectively. The values of \overline{M}_y for the several functional polyketones are given in Table 1.

Proton nuclear magnetic resonance

Proton Nuclear Magnetic Resonance 1H -NMR was used to determine the presence of the amino functionalization and molecular structures of each functional polyketone. The spectra were recorded at concentrations of

Table 1: Characteristics of EA and functional polyketones.

Functional polyketone	$Ne^{0.5}$ (g/g)	$Ne^{0.8}$ (g/g)	$X_{co}^{0.5}$ (%)	$X_{co}^{0.8}$ (%)	\overline{M}_y (g/mol)
PK30-BA	0.045	0.061	45	68	168
PK30-API	0.116	0.151	50	69	221
PK30-AEP	0.114	0.150	48	70	225
PK30-2DME	0.087	0.118	49	71	184
PK30-1,3DAP	0.085	0.108	50	68	198
PK30-DEE	0.081	0.103	50	69	212
PK30-1,2DAP	0.092	0.129	49	73	169
PK30-4PcA	0.097	0.112	60	74	204

$Ne^{0.5}$, Nitrogen content at predicted initial molar ratio of 0.5 between the amines and 1,4-dicarbonyl groups in the polyketone.

$Ne^{0.8}$, Nitrogen content at predicted initial molar ratio of 0.8 between the amines and 1,4-dicarbonyl groups in the polyketone.

$X_{co}^{0.5}$, 1,4-dicarbonyl conversion at $Ne^{0.5}$.

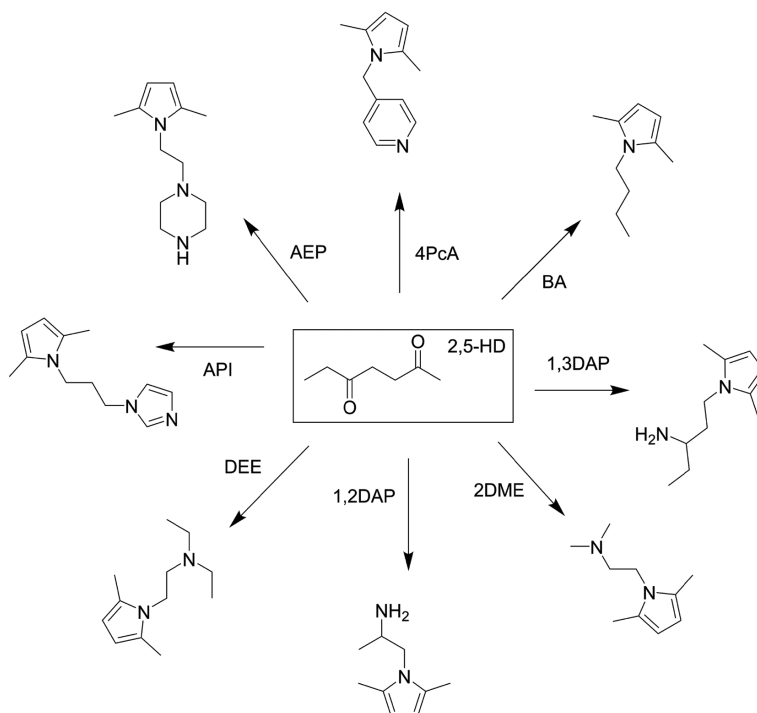
$X_{co}^{0.8}$, 1,4-dicarbonyl conversion at $Ne^{0.8}$.

\overline{M}_y , Average M_w reacted (functional) pyrrole repeating unit based at reactions of 1,4-dicarbonyl with amines.

50 mg/mL in DMSO- d_6 (Sigma-Aldrich $\geq 98\%$) on a Varian Mercury Plus 400 MHz spectrometer. Before the samples were transferred into the NMR-tube, they were filtered using Pasteur pipettes filled with glass wool in order to remove solid particles.

Model compounds by 1H -NMR

Model compounds were used as reference for guiding structure determination and determination of conversion rates of the amines. N-substituted 2,5-pyrrolediyl groups incorporated in the backbone bearing pendent amino functional groups, were synthesized by reacting 2,5-HD with the amines chosen here (Fig. 4). The

**Fig. 4:** Repeating units. Model compound reactions of 2,5-HD (Centered) with the amines.

model compound reactions (as substitute for the 1,4-dicarbonyl in PK30) were carried out in an NMR-tube with DMSO-d₆ at 80 °C. The reaction was started by adding the corresponding amount of 2,5-HD (34.2 mg) and the amines at equimolar ratio in 0.83 g of DMSO-d₆. Spectra of the reaction mixture were recorded at 30 min time intervals for 12 h in order to investigate the kinetic process of the reactions, directly indicating the conversion rate of the Paal-Knorr reaction.

Results and discussion

Synthesis and characterization of functional polyketones

The synthesized functional polyketones were recovered with liquid N₂ from the reactor after cooling down at room temperature. They all showed a relatively high viscosity and varied in color from light to dark brown. Samples were coded according the following nomenclature: PK30-mon, where mon represents the pending functionality, i.e. the amines. Table 1 shows the degrees of carbonyl conversion which are strictly a function of the N-content (Eq. 1). For example, the conversion of PK30-4PcA was found to be relatively high, 74 % with respect to the 1,4-dicarbonyl groups. The structures shown in Fig. 1 have either one (BA), two or three N-atoms. At least at the qualitative level, the *Ne* values in Table 1 agree with this observation. Whereas BA shows the lowest *Ne* value, API and AEP score the highest.

This observation is off course true if the correlation with each particular functional molecular-region is based on its N-content (chosen here for interacting-preference reasons) and not on a relatively total (similar) N-content of the functional polyketone.

Table 1 also shows two different N-content values in the polyketone, namely *Ne*^{0.5} and *Ne*^{0.8}. One represent the viable number of pyrrole rings able to react (*Ne*^{0.8}) [5], the other represent the desired number of reacted pyrrole rings (*Ne*^{0.5}) necessary to leave free reactive groups for cross-linking. The measured EA values (nitrogen content) clearly demonstrates the reaction of the amines with the backbone of the polymer although, obviously, it does not provide any specific information on the chemical structure, which was then investigated by ¹H-NMR. Since the ¹H-NMR spectra resulted in broad peaks, mainly due to the oligomeric nature of the products, a correct peak assignment was carried out by comparing the obtained spectra from the structures in Fig. 1 with those of the model compounds in Fig. 4. The peak positions shown in Fig. 5, correspond to the existence of the proton on the pyrrole ring pyr-*H* and protons attached on the molecular groups of the pyrrole ring $-CH_2-$, $=CH-$, $-NH-$, $-N(CH_3)_2$, $N(CH_2)_2$, $-NH_2$, $-CH_3$. For instance, the ppm values of positions 3, 6, 17, 21, 29, 33, and 44 are all, apart from 29, identical to the value of 5.7 ppm found for position 49 of the repeating unit after reaction with BA representing the H on the pyrrole ring. This interpretation clearly provides evidence of the actual formation of the functional polyketones from PK30.

Kinetics

Based on the ¹H-NMR spectra generated from model compounds (Fig. 4), the time dependent amine conversion (*X*) could be calculated by:

$$X = \frac{\text{integral area H reacted amine}}{\text{integral area H reacted amine} + \text{H unreacted amine}} \quad (7)$$

As an example, the conversions for API were found from the ratios of the integral peaks of the proton placed at the ortho position in the imidazole ring ($=CH-$) of the reacted and unreacted API within 6.939–6.822 ppm. The reaction follows a second order kinetics [27] and the data was analyzed accordingly to Eq. 8:

$$\frac{1}{X} = kt \quad (8)$$

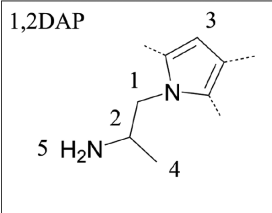
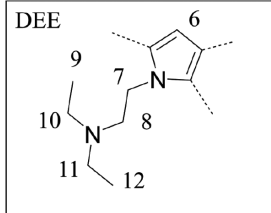
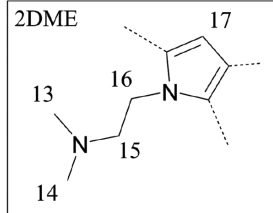
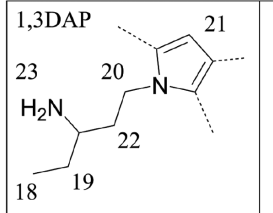
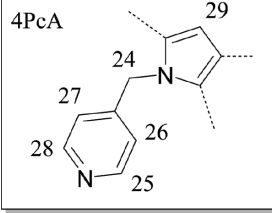
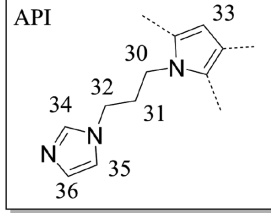
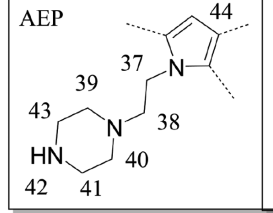
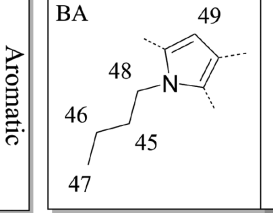
1,2DAP 	DEE 	2DME 	1,3DAP 	Aliphatic		
4PcA 	API 	AEP 	BA 	Aromatic		
				Control		
1- [4.4]	8- [2.7]	15-[2.5]	22-[1.5]	29-[5.0]	36-[6.9]	43-[2.3]
2- [2.9]	9- [0.8]	16-[3.7]	23-[1.1]	30-[4.0]	37-[3.7]	44-[5.7]
3- [5.7]	10-[2.7]	17-[5.7]	24-[5.6]	31-[1.9]	38-[2.3]	45-[1.7]
4- [1.0]	11-[2.7]	18-[0.6]	25-[8.4]	32-[3.6]	39-[2.4]	46-[1.4]
5- [1.5]	12-[0.8]	19-[1.5]	26-[6.6]	33-[5.7]	40-[2.4]	47-[0.7]
6- [5.7]	13-[2.7]	20-[3.9]	27-[6.6]	34-[7.6]	41-[2.3]	48-[3.6]
7- [3.7]	14-[2.7]	21-[5.7]	28-[8.4]	35-[7.2]	42-[0.9]	49-[5.7]
						ppm

Fig. 5: Characteristics of ^1H -NMR analysis. Proton concentrations are listed in between brackets for each functional group. For brevity, R , and unreacted monomeric groups (carbonyl, $\text{C}=\text{O}$) are not shown.

where k is the rate constant and can be obtained from the slope of the linear fit. Figure 6 shows the calculated k -values in relation to the molecular structure. To indicate the goodness of the fits, the yielded regression coefficients (r) are also given in the figure. The results clearly show that the molecular structure of the amines affects the kinetics. For instance, 2DME reacts almost 10 times faster than API. The employed model compound is a representative for the Paal-Knorr pyrrole synthesis [28] of functional polyketones. The reaction mechanism holds a double condensation reaction, including an initial nucleophile attack by the primary amino unit on the ketone (hemiaminal), followed by a second attack (pyrrole ring-formation). This

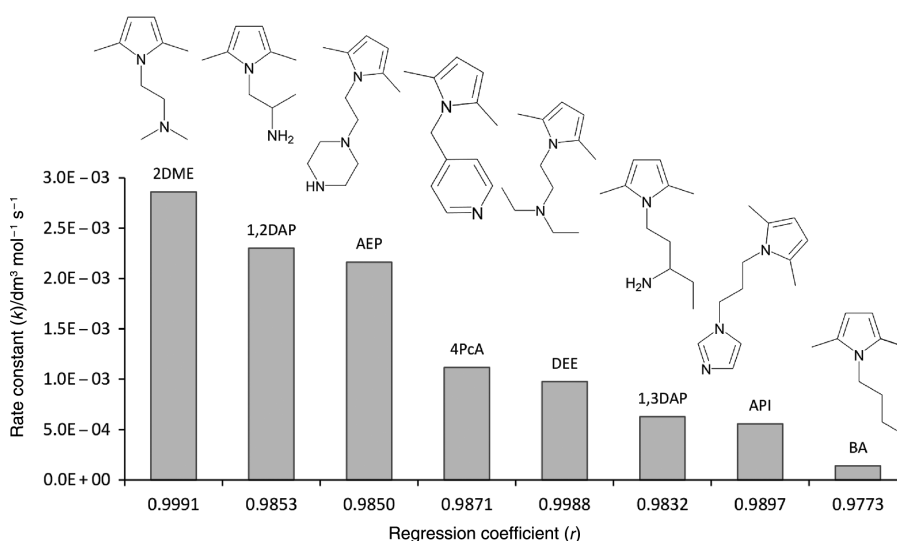


Fig. 6: k values for the linear fits of the kinetic data from the model compound reactions for the second order plots. Chemical structures above the bars represent the reacted amines.

means that for these reactions, the nucleophilic character of the amines [29] and the steric hindrance [5], both affect the k value.

For example, an amine with a primary pending-functionality displayed a higher k over a secondary pending-functionality (i.e. 1,2DAP to AEP). This result is in agreement with previous studies [23]. However, as can be noted, the nature of the type of amino functionality (i.e. aromatic and aliphatic) affected the accessibility of the amine to react. This could be clearly seen from the fact that an amine with an aromatic secondary pending-functionality showed a higher k over an aromatic amine with a tertiary pending-functionality (i.e. AEP to 4PcA). Furthermore, a relatively lower MW (Table 1) of the aromatic amines with a tertiary pending-functionality, resulted also in relatively higher k value (i.e. 4PcA to API). The same was observed with the aliphatic amines with a tertiary pending-functionality 2DME to DEE, and the aliphatic amines with a primary pending-functionality 1,2DAP to 1,3DAP. The reason for the faster kinetics of 2DME over 1,2DAP can most probably be attributed to the possibility for the amine to react at the β -position, which in turn could affect the transition rate from the hemiaminal to the pyrrole ring [30].

Conclusion

Employing the Paal-Knorr reaction, polyketones can be successfully chemically modified by reacting a class of amino compounds. A kinetic analysis revealed that the conversion rate depends on a number of defining structural parameters: steric hindrance, molecular weight and nucleophilicity. The obtained products are, after cross-linking, envisioned for the use of Ca^{2+} and Mg^{2+} removal from hard water. The functional characterization, i.e. the ability and capacity to adsorb Ca^{2+} and/or Mg^{2+} is the focus of Part II of this study.

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